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## JAPANESE / ENGLISH TRANSLATION OF

Japanese Patent Application JP 10 - 291225 A

Calendered Molded Sheet Composed of Polyester Resin Composition,  
and Manufacturing Method Thereof

Your Ref: 103003 - 15

For: Eastman Chemical Company

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**(54) [Title of the Invention]**

**Calendered Molded Sheet Composed of  
Polyester Resin Composition, and  
Manufacturing Method Thereof**

**(57) [Summary]**

**[Object]** To obtain a flexible molded sheet that is suited to calendering and has excellent productivity, heat resistance, chemical resistance, chemical transfer resistance, and mechanical properties.

**[Means of Achievement]** A molded sheet obtained by means of calendering a polyester resin composition comprising 100 parts by weight of a polyester block copolymer (A) whose melting point falls within a specific range, and 10 to 120 parts by weight of an aromatic crystalline

polyester resin (B) whose melting point is 20°C greater, wherein the polyester block copolymer comprises 20 to 50 wt% of a hard segment (a) composed of polybutylene terephthalate in which terephthalic acid and tetramethylene glycol account for 60 mol% or more of the total dicarboxylic acid, and of 80 to 50 wt% of a soft segment (b) composed of a polyester in which an aromatic dicarboxylic acid is contained in an amount of 60 mol% or greater relative to the total dicarboxylic acid component, and in which a diol as represented by  $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_i\text{H}$  ( $i = 2$  to 5) is contained in an amount of 60 mol% or greater relative to the total dicarboxylic acid.

### [Claims]

**[Claim 1]** A molded sheet obtained by means of calendering a polyester resin composition comprising 100 parts by weight of a polyester block copolymer (A) whose melting point ( $T_1$ ) satisfied equations (1) to (3) below

$$[\text{Numerical Equations 1}] T_0 - 5^\circ\text{C} > T_1 > T_0 - 60^\circ\text{C} \quad (1)$$

$$T_1 > T' + 10^\circ\text{C} \quad (2)$$

$$T_1 \leq 210^\circ\text{C} \quad (3)$$

[ $T_0$ : melting point of a polymer composed of the components that constitute the hard segment,  $T'$ : melting point of a random copolymer composed of all the components constituting the hard segment and the soft segment]

and 10 to 120 parts by weight of an aromatic crystalline polyester resin (B) whose melting point ( $T_2$ ) satisfies equation (4) below, wherein the polyester block copolymer comprises 20 to 50 wt% of a hard segment (a) composed of polybutylene terephthalate in which terephthalic acid and tetramethylene glycol account for 60 mol% or more of the total dicarboxylic acid, and 80 to 50 wt% of a soft segment (b) composed of a polyester in which an aromatic dicarboxylic acid is contained in an amount of 60 mol% or greater relative to the total dicarboxylic acid component and in which a diol as represented by  $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_i\text{H}$  ( $i = 2$  to 5) is contained in an amount of 60 mol% or greater relative to the total dicarboxylic acid component.

$$[\text{Numerical Equation 2}] T_2 - T_1 > 20^\circ\text{C} \quad (4)$$

**[Claim 2]** A molded sheet obtained by means of calendering a polyester resin composition comprising 100 parts by weight of a polyester block copolymer (A) whose melting point ( $T_1$ ) satisfied equations (1) to (3) below

$$[\text{Numerical Equations 3}] T_0 - 5^\circ\text{C} > T_1 > T_0 - 60^\circ\text{C} \quad (1)$$

$$T_1 > T' + 10^\circ\text{C} \quad (2)$$

$$T_1 \leq 210^\circ\text{C} \quad (3)$$

[ $T_0$ : melting point of a polymer composed of the components that constitute the hard segment,  $T'$ : melting point of a random copolymer composed of all the components constituting the hard segment and the soft segment]

and 10 to 120 parts by weight of polybutylene terephthalate (B') whose melting point ( $T_2$ ) satisfies equation (4) below, wherein the polyester block copolymer comprises 20 to 50 wt% of a hard segment (a) composed of polybutylene terephthalate in which terephthalic acid and tetramethylene glycol account for 60 mol% or more of the total dicarboxylic acid, and of 80 to 50 wt% of a soft segment (b) composed of a polyether ester in which an aromatic dicarboxylic acid is contained in an amount of 60 mol% or greater relative to the total dicarboxylic acid component, in which a diol as represented by  $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_i\text{H}$  ( $i = 2$  to 5) is contained in an amount of 60 mol% or greater relative to the total dicarboxylic acid component, and in which a polyoxyalkylene glycol with a molecular weight of 1200 or less is contained in an amount of 5 to 30 wt% relative to the total polyether ester.

$$[\text{Numerical Equation 4}] T_2 \geq 210^\circ\text{C} \quad (4)$$

[**Claim 3**] A method for the manufacture of a molded sheet as described in Claims 1 or 2, characterized in that calender molding is performed at a processing temperature ( $T_3$ ) that satisfies equation (5) below.

$$[\text{Numerical Equation 5}] T_1 - 10^\circ\text{C} < T_3 < T_2 \quad (5)$$

[ $T_2$ : melting point of the aromatic crystalline polyester resin]

### **[Detailed Description of the Invention]**

#### **[0001]**

**[Technological Field of the Invention]** The present invention relates to a molded sheet that is formed by means of calendering a polyester resin composition having rubber elasticity characteristics, and to a method for its manufacture. In greater detail, the invention relates to a molded sheet that is formed by means of calendering a polyester resin composition obtained as a result of compounding crystalline polyester resin compositions of different melting points with a specific polyester block copolymer having rubber elasticity, and to a method for its manufacture.

[0002]

**[Prior Art]** Conventionally, methods in which extrusion is performed using a T-die, and methods involving the use of calender molding have been used for molding sheet products. However, when moldings of a wide product range are to be obtained, calender molding is superior from the standpoint of manufacturing costs.

[0003] For this reason, flexible vinyl chloride sheets and olefin resin sheets are generally manufactured by means of calendering.

[0004] Because of higher demands for heat resistance, chemical resistance, chemical transfer resistance, and mechanical properties in recent years, the use of polyester elastomers in which the aforementioned properties can be kept at a high level in flexible molded sheets has increased.

[0005] Although polyester elastomers have various excellent properties, they have a single melting point and are prone to hydrolysis, for which reason they are not suited to calender molding in which prolonged melting and kneading are performed in an air atmosphere, so sheets are commonly molded using a T-die.

[0006] It is disclosed in JP (Kokai) 8-142290 that the processing temperatures can be lowered and that oxidative degradation and a hydrolysis-induced decrease in physical properties can be prevented as a result of using specific polyester elastomers whose melting points are lower than those of ordinary polyester elastomers in order to overcome the drawbacks of these polyester elastomers.

[0007]

**[Problems to Be Solved by the Invention]** Conventional polyester elastomers are aromatic polyester block copolymers, and the melting points of their hard segments are generally high, being 200°C or greater, for which reason processing is impossible unless the processing temperature is set at a minimum to 200°C or greater, and, preferably, to 220°C or greater.

[0008] This causes oxidative degradation and hydrolysis to occur and the properties of the polymer to undergo marked decrease at these processing temperatures. When the processing temperature exceeds the melting point of the hard segment, melt viscosity rapidly decreases, resin sagging and roll coiling occur, and processability and handling become poor.

**[0009]** An object of this invention is to discover a calenderable polyester resin composition and to obtain molded sheets that have excellent productivity, heat resistance, chemical resistance, chemical transfer resistance, mechanical properties, and flexibility.

**[0010]** As used herein, the term "calenderable polymers" refers to polymers for which processing temperatures can be lowered, in which there is little degradation of the polymer due to its heat history, which are of high viscosity at processing temperatures, and which are easy to handle and have good roll release characteristics.

**[0011]**

**[Means Used to Solve the Above-Mentioned Problems]** The inventors perfected this invention as a result of the discovery that polyester resin compositions that are obtained by means of compounding specific crystalline polyester resins with specific polyester block copolymers having rubber elasticity characteristics have superior heat resistance, can be calendered at low processing temperatures, and exhibit good roll release.

**[0012]** Specifically, this invention provides the following: [1] A molded sheet obtained by means of calendering a polyester resin composition comprising 100 parts by weight of a polyester block copolymer (A) whose melting point ( $T_1$ ) satisfies equations (1) to (3) below

**[0013]**

$$[Numerical\ Equation\ 6] T_0 - 5^\circ\text{C} > T_1 > T_0 - 60^\circ\text{C} \quad (1)$$

$$T_1 > T' + 10^\circ\text{C} \quad (2)$$

$$T_1 \leq 210^\circ\text{C} \quad (3)$$

[ $T_0$ : melting point of a polymer composed of the components that constitute the hard segment,  $T'$ : melting point of a random copolymer composed of all the components constituting the hard segment and the soft segment]

and 10 to 120 parts by weight of an aromatic crystalline polyester resin (B) whose melting point ( $T_2$ ) satisfies equation (4) below, wherein the polyester block copolymer comprises 20 to 50 wt% of a hard segment (a) composed of polybutylene terephthalate in which terephthalic acid and tetramethylene glycol account for 60 mol% or more of the total dicarboxylic acid, and of 80 to 50 wt% of a soft segment (b) composed of a polyester in which an aromatic dicarboxylic acid is contained in an amount of 60 mol% or greater relative to the total dicarboxylic acid component

and in which a diol as represented by  $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_i\text{H}$  ( $i = 2$  to  $5$ ) is contained in an amount of  $60$  mol% or greater relative to the total dicarboxylic acid component.

[0014]

[Numerical Equation 7]  $T_2 - T_1 > 20^\circ\text{C}$  (4)

[0015] [2] A molded sheet obtained by means of calendering a polyester resin composition comprising  $100$  parts by weight of a polyester block copolymer (A) whose melting point ( $T_1$ ) satisfies equations (1) to (3) below

[0016]

[Numerical Equations 8]  $T_0 - 5^\circ\text{C} > T_1 > T_0 - 60^\circ\text{C}$  (1)

$T_1 > T' + 10^\circ\text{C}$  (2)

$T_1 \leq 210^\circ\text{C}$  (3)

[ $T_0$ : melting point of a polymer composed of the components that constitute the hard segment,  $T'$ : melting point of a random copolymer composed of all the components constituting the hard segment and the soft segment]

and  $10$  to  $120$  parts by weight of polybutylene terephthalate (B') whose melting point ( $T_2$ ) satisfies equation (4) below, wherein the polyester block copolymer comprises  $20$  to  $50$  wt% of a hard segment (a) composed of polybutylene terephthalate in which terephthalic acid and tetramethylene glycol account for  $60$  mol% or more of the total dicarboxylic acid, and of  $80$  to  $50$  wt% of a soft segment (b) composed of a polyether ester in which an aromatic dicarboxylic acid is contained in an amount of  $60$  mol% or greater relative to the total dicarboxylic acid component, in which a diol as represented by  $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_i\text{H}$  ( $i = 2$  to  $5$ ) is contained in an amount of  $60$  mol% or greater relative to the total dicarboxylic acid component, and in which a polyoxyalkylene glycol with a molecular weight of  $1200$  or less is contained in an amount of  $5$  to  $30$  wt% relative to the total polyether ester.

[0017]

[Numerical Equation 9]  $T_2 \geq 210^\circ\text{C}$  (4)

A method for their manufacture is also provided. This invention will now be described in detail.

[0018] [Polyester block copolymer (A)]

[Hard segment (a)]

The hard segment (a) of the polyester block copolymer (A) that is used in this invention is polybutylene terephthalate in which terephthalic acid and tetramethylene glycol are present in amounts of 60 mol% or greater relative to the total dicarboxylic acid.

[0019] The polybutylene terephthalate may be copolymerized with aromatic dicarboxylic acids that contain benzene rings or naphthalene rings, aliphatic dicarboxylic acids with 4 to 12 carbon atoms, diols such as aliphatic diols with 2 to 12 carbon atoms other than tetramethylene glycol, and alicyclic diols such as cyclohexene dimethanol. The copolymerization proportion should be 40 mol% or less, and, preferably, 30 mol% or less, relative to the total dicarboxylic acid component. This copolymerization proportion is preferred because the melting point increases with increased proportion. Copolymerization is also performed for the purpose of ensuring increased flexibility. However, when the compounding proportion is high, crystallization is impaired and moldability and other properties are adversely affected, for which reason the proportion should not be too high. The copolymerization proportion should be such that the melting point ( $T_0$ ) of the hard segment crystals is 160°C or higher, and, preferably, 170°C or higher.

[0020] [Soft segment (b)]

On the other hand, the soft segment is a polyester in which the aromatic dicarboxylic acid accounts for 60 mol% or greater relative to the total dicarboxylic acid component and in which a diol component represented by  $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_i\text{H}$  ( $i = 2$  to 5) accounts for 60 mol% or greater relative to the total dicarboxylic acid component.

[0021] This polyester soft segment may be a substance obtained by means of copolymerizing an aromatic dicarboxylic acid other than terephthalic acid, an aliphatic or alicyclic dicarboxylic acid, or a short-chain diol. The copolymerization proportion should be 40 mol% or less relative to the total dicarboxylic acid component. When the copolymerization component exceeds 40 mol%, heat resistance is adversely affected.

[0022] Examples of suitable copolymerizable aromatic dicarboxylic acids, aliphatic dicarboxylic acids, and alicyclic dicarboxylic acids include isophthalic acid, phthalic acid, naphthalene dicarboxylic acids, straight-chain dicarboxylic acids with 4 to 12 carbon atoms, and, in particular, straight-chain dicarboxylic acids with 8 to 12 carbon atoms and cyclohexane dicarboxylic acids.

[0023] As described above, the diol component that constitutes the hard-segment polyester is a diol represented by  $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_i\text{H}$ , in which  $i = 2$  to 5. When the  $i$ -value is 1, the molded sheet has high hardness, and when the  $i$ -value is 6 or greater, the hygroscopicity of the molded sheet is increased and the composition is not suitable for use in this invention. Preferably, the  $i$ -value should be 3 to 4.

[0024] Further, the flexibility of the polyester block copolymer at low temperatures can be improved as a result of using a polyether ester copolymer obtained by means of copolymerizing a polyoxyalkylene glycol component with the aforementioned polyester polymer as the soft-segment polyester. From the standpoint of compatibility with the polybutylene terephthalate, which is the hard segment, the molecular weight of the polyoxyalkylene glycol component should be 1200 or less, and, preferably, 1000 or less. Its molecular weight is preferably 400 or greater, and, particularly, 500 or greater. Copolymerization of the polyoxyalkylene glycol in an amount of 5 to 30 wt% relative to the total polyester block copolymer (A) is preferable because it improves low temperature properties, with 5 to 20 wt% being even more preferable.

Copolymerizing this polyoxyalkylene glycol component in the range described above is preferable for improving low temperature properties. When a large quantity is used, chemical resistance and heat resistance are decreased. This is not desirable.

[0025] The polyoxyalkylene glycol may be a substance having repeating units with 2 to 4 carbon atoms, with polytetramethylene glycol being particularly preferable.

[0026] The weight ratio (wt% ratio) of the hard and soft segments should be between 20 to 50 and 80 to 50, and, preferably, between 25 to 40 and 75 to 60. When the ratio of the hard segment in the polyester block copolymer that is obtained is greater than this, problems are encountered because the product acquires high hardness and becomes difficult to use. On the other hand, when the ratio of the soft segment is greater than this, crystallinity decreases and molding becomes difficult.

[0027] The lengths of the soft and hard segments of the polyester block copolymer (A), expressed as molecular weights, are preferably 500 to 7000, and, more preferably, 800 to 5000. Direct measurement of the segment lengths is difficult. For example, the composition of the polyester that constitutes the soft segment, and the composition of the polyester that constitutes the hard segment, can be estimated from the melting point ( $T_0$ ) of the polyester composed of the

components constituting the hard segment, and the melting point ( $T_1$ ) of the resulting polyester block copolymer by means of using Flory's equation.

[0028] Based on this point, the melting point ( $T_1$ ) of the polyester block copolymer (A) is an important term in the equation. The melting point ( $T_1$ ) should be in the range from  $T_0 - 5^\circ\text{C}$  to  $T_0 - 60^\circ\text{C}$ , preferably, in the range from  $T_0 - 10^\circ\text{C}$  to  $T_0 - 50^\circ\text{C}$ , and, more preferably, in the range from  $T_0 - 15^\circ\text{C}$  to  $T_0 - 40^\circ\text{C}$ . Here,  $T_0$  is the melting point of the polymer composed of the component that constitutes the hard segment.

[0029] It is necessary for the melting point ( $T_1$ ) to be  $10^\circ\text{C}$  higher than the melting point ( $T'$ ) of the random copolymerization polymer composed of all the components that constitute the hard segment and the soft segment, and it is preferable that the temperature be  $20^\circ\text{C}$  higher. When the melting point ( $T'$ ) of the random copolymer is indeterminate, the melting point ( $T_1$ ) is preferably set to  $150^\circ\text{C}$  or higher, and, more preferably, to  $160^\circ\text{C}$  or higher. However, in order for the effects of this invention to be achieved, the melting point ( $T_1$ ) must be less than  $210^\circ\text{C}$ , and is preferably less than  $200^\circ\text{C}$ .

[0030] When the polymer that is used in this invention is not a block copolymer but is rather a random copolymer, this random copolymer is amorphous, has a low glass transition temperature without having a melting point, and is in a jelly-like state at room temperature. When an attempt is made to form the polymer into a sheet, it becomes coiled on the rollers, and the resulting product cannot be used because of such practical problems as the formation of adhesive surfaces or the occurrence of a so-called blocking phenomenon in which the sheets adhere to each other. When the random copolymer does not have a melting point,  $T'$  can be considered to be  $0^\circ\text{C}$ .

[0031] The polyester block copolymer can be manufactured by means of a method in which the polymers that constitute the soft segment and the hard segment are manufactured separately and are then melted and mixed so that the melting point is lower than that of the polyester that constitutes the hard segment. This melting point varies depending on the mixing temperature and time. Therefore, at the time the material reaches a state in which the target melting point is achieved, a catalysis deactivator such as a phosphorus oxy acid should be added to deactivate the catalyst and to allow the resulting material to be used in the invention.

[0032] The polyester block copolymer (A) of this invention should have an intrinsic viscosity (measured at 35°C in o-chlorophenol) of 0.6 or greater, and, preferably, 0.8 to 1.5. A lower intrinsic viscosity is undesirable because a lower strength results.

[0033] The aromatic crystalline polyester resin (B) used in this invention is composed of an aromatic dicarboxylic acid and a diol. This crystalline polyester satisfies the relation  $T_2 - T_1 > 20^\circ\text{C}$ , where  $T_1$  is the melting point of the aforementioned polyester block copolymer (A), and  $T_2$  is the melting point of the aromatic crystalline polyester resin. At a difference in melting points of less than 20°C, the range of processing temperatures narrows, the viscosity decreases, roll coiling and other undesirable phenomena occur, and processability is adversely affected.

[0034] The aromatic dicarboxylic acid that constitutes the aromatic crystalline polyester resin (B) may be terephthalic acid or isophthalic acid, and the diol component is preferably a straight-chain aliphatic diol with 2 to 12 carbon atoms, such as polyoxyalkylene glycol.

[0035] A third component may be copolymerized with the aromatic crystalline polyester in small proportions (for example, ---- mol% or less or ----<sup>1</sup> mol% or less). The third component can be an aliphatic dicarboxylic acid (for example, adipic acid, sebacic acid, etc.), alicyclic dicarboxylic acid (for example, cyclohexane dicarboxylic acid), or aromatic diol (for example, hydroquinone).

[0036] In order to obtain the effect of this invention, the aromatic crystalline polyester resin (B) should have a high melting point and high crystallinity. From this standpoint, polybutylene terephthalate is preferable.

[0037] The proportion in which the aromatic crystalline polyester resin (B) is compounded with the polyester block copolymer (A) should be 10 to 120 parts by weight, and, preferably, 20 to 80 parts by weight, of aromatic crystalline polyester resin (B) per 100 parts by weight of polyester block copolymer (A). A lower proportion is ineffective for improving calender molding. When the proportion of aromatic crystalline polyester resin (B) is greater than 120 parts by weight, the processing temperature cannot be raised, plasticization defects occur, and the effect of the invention is evident.

[0038] Further, it is preferable to add known antioxidants, for example, hindered phenols, phosphites, thioethers, and amines, to the composition of this invention (which comprises polyester block copolymer (A) and aromatic crystalline polyester resin) for the purpose of inhibiting thermal degradation during processing.

[0039] Further, a known light resistance agents, for example, a hindered amine, benzotriazole or benzophenone, can be added for the purpose of improving the weather resistance of the molded sheets.

[0040] Similarly, stabilizers such as carbodiimide can be added to improve thermal degradation properties. In addition, aliphatic ester waxes, aliphatic metal salts, and polyethylene wax can be added within ranges that do not impair the effect of the invention for the purpose of improving processability.

[0041] Further, fillers, reinforcing agents, plasticizers, pigments, colorants, or other polymer that do not impede the stated objectives can be added in any desired proportion.

[0042] The calender molding that is used in this invention is a generally known method in which resin is held in the space between calender rolls at high temperature, where it is plasticized, kneaded, and then calendered to a specific thickness between the rolls. The processing temperature at this time, i.e., the calender roll temperature, must be in a range that satisfies equation (4) below.

[0043]

[Numerical Equation 10]  $T_1 - 10^\circ\text{C} < T_3 < T_2$  (4)

[ $T_1$ : melting point of the polyester block copolymer (A);  $T_2$ : melting point of the aromatic crystalline polyester resin (B);  $T_3$ : processing temperature (roll temperature)]

[0044] When the processing temperature is below this temperature, plasticization becomes poor, and, when it is above this temperature, thermal degradation becomes intense and release of the resin from the rolls becomes difficult. When waxes are added in an excess in order to improve the release properties at this time, there is the danger that the superior properties of the polyester resin composition will be impaired, for which reason this approach cannot be regarded as a suitable method.

[0045] In addition, other materials and sheet-like products can be introduced and composites such as laminates can be made in processes such as plasticization, coarse molding, calendering, and cooling. The rolls can comprise four or five rolls with a reverse L-shape or regular L-shape.

[0046] In this invention, the polyester resin composition may be kneaded in advance with these components before calender molding. The kneading method is generally continuous kneading in

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<sup>1</sup> Translator's note: These spaces are actually left blank in the original.

an extruding machine. With the objective of preventing degradation due to hydrolysis during processing, the resin composition may be dried in advance with hot air before being processed.

**[0047]**

**[Working Examples]** This invention will now be described in further detail by means of working examples. In the working examples, "parts" indicates parts by weight. The elastomers and the methods of measurement of physical properties used in the working examples and comparative examples are described below.

**[0048] [Elastomer 1]**

175 parts of dimethyl isophthalate, 23 parts of dimethyl sebacate, and 140 parts of hexamethylene glycol were subjected to a transesterification reaction with dibutyl tin diacetate catalyst, after which condensation polymerization was performed under reduced pressure, yielding an amorphous polyester (a) that had an intrinsic viscosity of 1.06 and was devoid of an endothermic peak attributable to melting of crystals by DSC. Polyethylene terephthalate chips ( $T_0 = 223^\circ\text{C}$ ) (b) that had an intrinsic viscosity of 0.98 and had been obtained separately in the same way as a result of a condensation polymerization were dried, 107 parts was added to the former polyester, and a further reaction was carried out for 45 minutes at  $240^\circ\text{C}$ , after which 0.1 parts of phenyl phosphinic acid was added and the reaction was stopped. This polyester block copolymer was collected and made into chips to serve as a raw material. The melting point of these chips was  $190^\circ\text{C}$  and their intrinsic viscosity was 0.93. The random copolymer composed of all the components described above did not have a melting point, and its melting point ( $T'$ ) was therefore considered to be  $0^\circ\text{C}$ .

**[0049] [Elastomer 2]**

194 parts of dimethyl terephthalate and 160 parts of triethylene glycol were subjected to a transesterification reaction with dibutyl tin acetate catalyst, after which condensation polymerization was performed under reduced pressure, yielding a jelly-like polyester (a) with an intrinsic viscosity of 0.76. Polyethylene terephthalate chips ( $T_0 = 223^\circ\text{C}$ ) (b) with an intrinsic viscosity of 0.98 that had been obtained separately in the same way as a result of a condensation polymerization were dried, 107 parts was added to the former polyester, a further reaction was carried out for 75 minutes at  $250^\circ\text{C}$ , 0.1 parts of phenyl phosphinic acid was added, and the reaction was stopped. The polyester block copolymer was collected and made into chips to serve

as a raw material. The melting point of the chips was 176°C, and their intrinsic viscosity was 0.83. The random copolymer composed of all the components described above did not have a melting point, and its melting point (T') was therefore considered to be 0°C.

**[0050] [Elastomer 3]**

245 parts of dimethyl terephthalate, 399 parts of polytetramethylene glycol (average molecular weight: 2000), and 159 parts of tetramethylene glycol were polymerized by means of a standard method using tetrabutoxytitanate as the catalyst, and a polyester block copolymer with an intrinsic viscosity of 1.42 and a hard segment content of 38 wt% was obtained. The hard segment content was found from the amount in which polytetramethylene glycol was introduced for polymerization in relation to the weight of the polymer after polymerization. The melting point of this polymer was 198°C.

**[0051] [Elastomer 4]**

613 parts of dimethyl terephthalate, 185 parts of polytetramethylene glycol (average molecular weight: 1000), and 398 parts of tetramethylene glycol were polymerized by means of a standard method using tetrabutoxytitanate as the catalyst, and a polyester block copolymer with an intrinsic viscosity of 1.61 and a hard segment content of 79 wt% was obtained. The melting point of this polymer was 216°C.

**[0052] [Aromatic crystalline polyester 1]**

Polybutylene terephthalate (PBT): Manufactured by Teijin Ltd.; brand name, C7000; melting point, 223°C

**[0053] [Aromatic crystalline polyester 2]**

375 parts of dimethyl terephthalate, 63 parts of dimethyl sebacate, and 438 parts of tetramethylene glycol were polymerized by means of a standard method using tetrabutoxytitanate as the catalyst, and a crystalline polyester resin with a melting point of 204°C was obtained.

**[0054] [Thermal stabilizer]**

Hindered phenol thermal stabilizer (Irganox 1010, manufactured by Ciba-Geigy)

**[0055] [Method of measuring melting point]**

A differential scanning calorimeter was used, and the endothermic peak temperature accompanying melting of the crystal structure was taken as the melting point (Tm) in accordance with JIS K7121.

**[0056] [Evaluation of thermal degradation]**

MFR values were determined before and after molding, and the decrease in molecular weight attributable to thermal degradation in the molding process was taken as the criterion. MFR was measured at a temperature of 240°C and at a load of 2160 g after the sample had been dried for 4 hours or longer at 130°C, and the amount of increase in the MFR value after molding in relation to the MFR value before molding was expressed as a percentage. Determination of MFR was based on JIS K7210.

**[0057] [Calender molding]**

1) The raw materials were introduced between two rolls with a diameter of 18 inches (for roll widths, see the working examples and comparative examples; clearance: 3 mm), and plasticization was performed.

2) The raw materials were then fed to four reverse L-shaped rolls and were made into a rolled sheet, with a 500 µm sheet sample finally being obtained. This was performed at a processing speed of 10 mm/minute.

**[0058] [Evaluation of moldability in calender molding]**

Visual evaluations were made of the state of plasticization (to determine whether the plasticization process was uniform and rapid) and the roll release characteristics (to determine whether the calendering process could be performed without affixation to plasticizing rolls and calender rolls)

**[0059] [Working Examples 1 to 5 and Comparative Examples 1 to 6]**

Sheets were calender molded with the compositions and under the conditions described in Table 1. The results are shown in Table 1. As should be evident from the results in Table 1, in Working Examples 1 to 5, the range of processing temperatures was on the order of 20°C and it was possible to lower the processing temperatures to less than 200°C, for which reason stable production was possible without thermal degradation.

[0060] When polymers were used alone in Comparative Examples 1 and 2, the processing temperature range was narrow, there was insufficient plasticization below the melting point, viscosity decreased sharply above the melting point, and sheet feeding was difficult to achieve without affixation to the calender roll.

[0061] In Comparative Examples 3 and 4, the effect of this invention was not evident even though polymers of different melting points were compounded.

**[0062]** In Comparative Example 5, the difference between the melting points of the two polymers was less than 20°C, for which reason the processing temperature range was narrowed, plasticization was poor, and adhesion to some rolls was observed.

**[0063]** In Comparative Example 6, there were good plasticization properties, improved release properties, and a reduced viscosity decrease due to thermal degradation at a processing temperature of 190 to 200°C. However, the molded sheet underwent surface peeling, physical properties were markedly decreased, and the quality was at a level that could not tolerate practical use.

**[0064]** Elastomer 3 used in Comparative Example 6 was an ester-ether elastomer widely available on the market. When the quantity of the soft segment was increased in order to decrease the melting point of this type of elastomer, compatibility with PBT was markedly decreased and the physical properties were adversely affected, indicating that the elastomer was unsuitable for obtaining the effect of the present invention.

**[0066]**

**[Effect of the Invention]** This invention can yield a flexible molded sheet that is suited to calender molding and has excellent productivity, heat resistance, chemical transfer resistance, and mechanical properties.

[0065]

[Table 1]

Composition (wt%)	Ex1	Ex2	Ex3	Ex4	Ex5	CmpEx1	CmpEx2	CmpEx3	CmpEx4	CompEx <sub>5</sub>	CmpEx6
Elastomer 1 (T <sub>m</sub> =190°C)	60	80								80	
Elastomer 2 (T <sub>m</sub> =176°C)		60	80	60				95	20		
Elastomer 3 (T <sub>m</sub> =195°C)					100					60	
Elastomer 4 (T <sub>m</sub> =216°C)					100						
Crystalline Pes1 (T <sub>m</sub> =223°C)	40	20	40	20				5	80		40
Crystalline Pes2 (T <sub>m</sub> =203°C)					40					20	
Thermal stabilizer	0.5phr	0.5phr	0.5phr	0.5phr	0.5phr	0.5phr	0.5phr	0.5phr	0.5phr	0.5phr	0.5phr
Processing temperature 170°C	VscDcr	-	3%	2%	3%	-	-	3%	-	-	-
Plistcz	RlsChr	-	-	Good	Good	-	-	Good	-	-	-
VscDcr	NPI	NPI	PrPI	PrPI	NPI	NPI	PrPI	NPI	NPI	NPI	NPI
Processing temperature 180°C	VscDcr	-	3%	3%	4%	-	-	3%	-	-	-
RlsChr	-	-	Good	Good	Good	-	-	Partial adhesion	-	-	-
Plistcz	NPI	NPI	Good	Good	Good	NPI	NPI	Good	NPI	NPI	NPI
VscDcr	6%	8%	5%	4%	6%	2%	-	5%	-	3%	4%
Processing temperature 190°C	RlsChr	Good	Good	Good	Good	Good	-	Release difficult	-	Partial adhesion	Good
Plistcz	Good	Good	Good	Good	Good	PrPI	NPI	Good	NPI	Good	PrPI
VscDcr	5%	10%	11%	14%	9%	9%	-	13%	-	16%	14%
Processing temperature 200°C	RlsChr	Good	Good	Good	Good	Partial adhesion	-	Release difficult	-	Release difficult	Good
Plistcz	Good	Good	Good	Good	Good	Good	NPI	Good	NPI	Good	Good
VscDcr	24%	33%	38%	42%	34%	26%	23%	42%	-	-	-
Processing temperature 210°C	RlsChr	Partial adhesion	Partial adhesion	Release	Release	Good	Release	Good	-	-	Partial adhesion
Plistcz	Good	Good	Good	Good	Good	PrPI	Good	PrPI	NPI	-	Good
VscDcr	47%	54%	51%	58%	-	-	32%	55%	12%	-	23%
Processing temperature 220°C	RlsChr	Release difficult	Release difficult	Release difficult	Release difficult	-	Release difficult	Good	-	Release difficult	-
Plistcz	Good	Good	Good	Good	Good	-	Good	Good	PrPI	-	Good

Thermal stabilizer: hindered phenolic thermal stabilizer (Irganox 1010, manufactured by Ciba-Geigy)

Abbreviations: VscDcr = Viscosity decrease; RlsChr = Release characteristics; Plistcz = Plasticization; NPI = not plasticized; PrPI = Partial plasticization